Etch-stop characteristics of Sc_2O_3 and HfO_2 films for multilayer dielectric grating applications

J. A. Britten,[a] H. T. Nguyen, S. F. Falabella, B. W. Shore, and M. D. Perry
Lawrence Livermore National Laboratory, Livermore, California 94550

D. H. Raguin
Rochester Photonics Corp., Rochester, New York 14623

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High-efficiency, high laser-damage threshold reflection gratings can be made by etching a grating structure into the top layer of a multilayer high-reflectivity stack. Spatial efficiency and wave-front uniformity can be maximized by taking advantage of the etch-stop properties of the layer underneath the top layer to be etched. The etch-stop layer must have a high optical damage resistance, which places severe restrictions on available materials. The etch characteristics of HfO_2 and Sc_2O_3, two materials commonly used in high laser-damage optical coatings, have been evaluated. The etch rate selectivities of e-beam evaporated $SiO_2/HfO_2/Sc_2O_3$ thin films in a reactive ion etching system optimized for SiO_2 etching are approximately 100/10/1. Gratings etched to a HfO_2 etch-stop layer suffered from deposition of fluorinated Hf compounds on the SiO_2 grating sidewalls, but sidewalls were clean when Sc_2O_3 was used as the etch-stop layer.

The technique of chirped-pulse amplification (CPA) for producing ultrahigh intensity, ultrashort pulse lasers[1,2] employs large-aperture diffraction gratings to compress amplified pulses down to subpicosecond pulse lengths. These gratings must be highly efficient, since the laser pulse diffracts from a grating surface four times in a typical compressor scheme. The gratings must have a high optical damage threshold as well. Gratings exhibiting high efficiency and high tolerance to optical damage are useful in other laser applications, such as wavelength tuning elements in laser cavities. Multilayer dielectric gratings[3] (MDGs) have both higher diffraction efficiencies (albeit for narrow bandwidths) and higher laser damage thresholds than the gold-overcoated gratings presently used in high-power CPA lasers. In these gratings, interference effects from alternating layers of low and high-index dielectric materials provide high reflectivity at a given use angle, wavelength, and polarization, and a grating structure of sufficiently small period relative to the laser wavelength, etched into the top dielectric layer, provides high diffraction efficiency in the -1 order. We have designed and fabricated small-scale MDGs with greater than 95% diffraction efficiency,[4,5] and which exceed the laser damage threshold of gold-overcoated gratings.[5]

A design goal for these gratings is that their efficiency be robust with respect to etch rate variations across large areas. High efficiency designs are possible by etching a grating structure completely through a relatively thick (>650 nm) SiO_2 layer atop a multilayer stack consisting of alternating layers of SiO_2 and a high-index dielectric.[5] This design requires that the high-index layer be resistant to the SiO_2 etch conditions. The most important criterion for the high-index layer, however, is that it possess a high optical damage threshold. Hafnia (HfO_2) is typically the high-index material of choice for multilayer high reflectors for high-power lasers.[6] It has also been reported to act as an effective stop etch layer when etching SiO_2 overcoats.[7] We have fabricated HfO_2/SiO_2 MDGs in which the top HfO_2 layer is the etch stop for a thick SiO_2 grating layer. These gratings exhibited growth of columnar fine structures, apparently from sputtered HfO_2 during the etch process, on the SiO_2 grating sidewalls.[5] An example of an etched grating on which these deposits began to appear is shown in Fig. 1. For gratings that were overetched by about a factor of 2, these columnar growths grew to completely envelop the SiO_2 grating ridge. Energy dispersive spectroscopy on an overetched grating showed the presence of fluorine in amounts of up to 5 wt %. These columnar structures did not form when HfO_2 films were etched through a photoresist-only mask, leading to the conclusion that an SiO_2 surface was required for a significant sticking probability of this sputtered fluorinated hafnium compound. The amount of growth varies as a function of processing parameters but is always apparent when HfO_2 is used as the etch-stop layer. These growths contributed to unacceptable scatter losses from the gratings, and the sharp edges concentrate electric fields and reduce laser damage thresholds.

It is desirable to replace HfO_2 with an alternative material that has a high refractive index, etch-stop properties and a high optical damage resistance. Scandia (Sc_2O_3) possesses perhaps the highest laser-damage threshold of any high-index oxide. It has been used with SiO_2 to produce damage-resistant multilayer optical coatings for UV light,[8,9] and its damage-resistance characteristics at 1.05 μm are equally good. Evaporated scandia has a slightly lower refractive index (1.8) than hafnia (1.9), and has similar deposition characteristics. Scandia differs from hafnia mainly in its solubility in acidic solutions, a property that has been exploited in making lift-off layers for multilayer dielectric coatings.[10]

[a]Electronic mail: britten1@llnl.gov

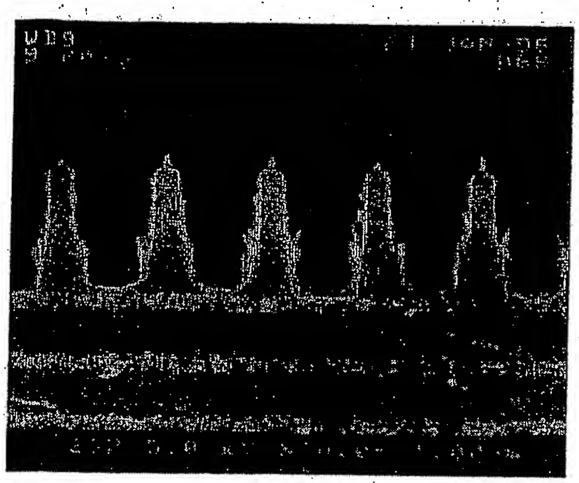

FIG. 1. Multilayer dielectric grating with 0.67 μm pitch grating etched by RIE through 750 nm of evaporated SiO_2 to a HfO_2 etch-stop layer. Note the growth of columnar structures on the sidewall and top that are believed to be sputtered fluorinated Hf compounds (9-20-3).

However, its etching properties are apparently unreported. We describe here a comparative study of the etch rates of electron-beam evaporated SiO_2, HfO_2, and Sc_2O_3 under conditions typical of SiO_2 etching in RIE and RIBE systems. We also show results of etch-stop trials of Sc_2O_3 films underlying submicron-pitch grating structures etched into SiO_2.

The thin film coatings were prepared by electron-beam evaporation onto glass microscope slides. Etch rates were determined by patterning coarse features into photoresist films spun onto these slides, subjecting the samples to the etch process, stripping the resist mask, and measuring step heights by atomic force microscopy and contact profilometry. Two etching systems were used: a plasmatherm RIE and a chemically assisted ion beam etcher using a 5 cm Kaufmann ion source. The processing conditions are typical for etching SiO_2.

Figure 2 shows measured etched depth vs etching time for the RIE system, using identical processing conditions optimized for high SiO_2 etch rates. It is apparent that scandia is much more resistant to etching than hafnia. The etch rate selectivities of $SiO_2/HfO_2/Sc_2O_3$ are approximately 100/10/1, respectively. The etch rate selectivity of SiO_2/HfO_2 of 10/1 agrees fairly well with the 16/1 value reported by Shih *et al.*[7]

TABLE I. Nominal etch rates for SiO_2, HfO_2, and Sc_2O_3 for SiO_2 etch conditions in RIE and RIBE systems. RIE conditions: 40 mTorr, 50 sccm reactive gas, 4.4% O_2, 95.6% CHF_3, and 150 W RF. RIBE conditions: 0.325 mTorr, 3.25 sccm at 61% Ar, 31% CHF_3, 8% O_2, 200 V beam voltage, and 10 mA beam current.

Etch rate (nm/min)	SiO_2	HfO_2	Sc_2O_3
RIE	54.8	5.5	0.5
RIBE	11.2	4.2	0.8

Table I summarizes these values and compares them with etch rates measured after RIBE processing. In the RIBE configuration, O_2 and CF_3 were introduced along with Ar into the ionization source, and the resulting multicomponent ion beam was directed to the work piece. The RIBE process suffers from decreased selectivity due to a larger sputtering component, but is of interest in that larger parts can be etched. The etch rate selectivity of SiO_2 to Sc_2O_3 in this system is still rather good at about 14/1.

Figure 3 shows a 0.67 μm period grating structure etched about 700 nm down through evaporated SiO_2 to a Sc_2O_3 stop-etch layer. This sample was etched in the RIE system using processing conditions described in Table I. The grating sidewalls look markedly cleaner than ones in which HfO_2 stop layers were utilized. Our theoretical design codes[5,11] show that high-efficiency MDG designs are possible for either material as the stop-etch layer, and as a consequence, superior structures can be made using Sc_2O_3 as the stop layer. For example, Fig. 4 plots the calculated diffraction

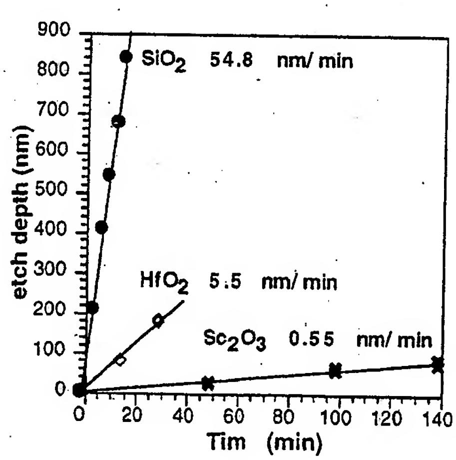

FIG. 2. Measured etch depths vs time for RIE processing of SiO_2, HfO_2, and Sc_2O_3.

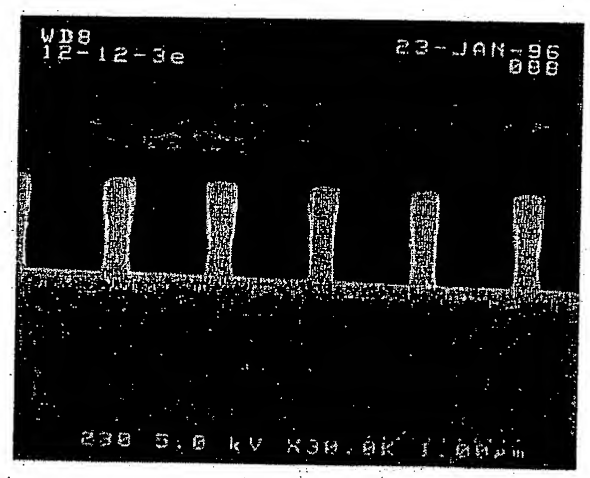

FIG. 3. SiO_2 grating profiles at 0.66 μm pitch, etched 700 nm down to a Sc_2O_3 stop-etch layer in a RIE system (12-12-3*e*).

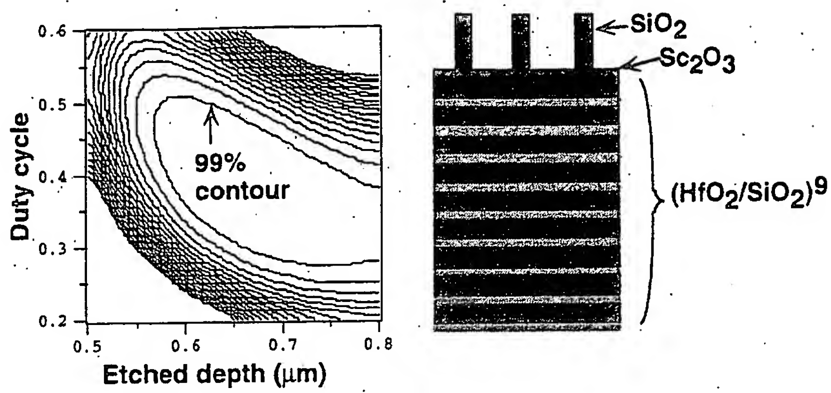

FIG. 4. Theoretical diffraction efficiency for 1.05 μm light at 52°, as a function of grating depth and duty cycle, for gratings etched completely through a SiO_2 layer to a Sc_2O_3 stop layer atop a HfO_2/SiO_2 stack. Maximum predicted diffraction efficiency >99%.

efficiency for 1.05 μm light at 52° as a function of grating depth and duty cycle (the fraction of the grating period comprising the grating ridge) for rectangular gratings on a 0.67 μm pitch etched completely through a SiO_2 layer to a Sc_2O_3 stop layer. The grating and the stop layer sit atop a nine layer–pair HfO_2/SiO_2 stack. It is seen that with this design high efficiencies (>99% in theory) can be attained over a rather broad range of SiO_2 grating depth and duty cycle. We are in the process of fabricating witness gratings of this design.

To summarize, etch rate selectivities of $SiO_2/HfO_2/Sc_2O_3$ in a RIE system optimized for etching SiO_2 are approximately 100/10/1, respectively, while in a RIBE system with a higher sputtering component, the selectivities are approximately 14/5/1. When HfO_2 is used as an etch stop layer, adhesion of relatively nonvolatile sputtered hafnium/fluoride compounds onto the SiO_2 grating sidewalls occurs during the etch. When Sc_2O_3 is used as the etch stop layer, SiO_2 sidewalls remain relatively clean. Since high-efficiency grating designs are possible using either material, scandia is, therefore, the preferred etch stop layer for MDGs.

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